

A NOVEL APPROACH TO GASIFICATION OF COAL
USING CHEMICALLY INCORPORATED CATALYSTS

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INTRODUCTION

Battelle's Columbus Laboratories is developing new approaches to gasification of coal, with ERDA sponsorship, using known gasification catalysts that are chemically incorporated into the coal. The chemical incorporation of a catalyst is achieved by treating the coal with the catalyst and water at elevated temperatures and pressures, usually in the presence of an aqueous alkali solution. The process is a modification of the proprietary Hydrothermal Coal Process for reducing the sulfur content of coal (1).

Earlier work on chemical incorporation of gasification catalysts was done with in-house funds using the "so-called" power-plant grind or 70 percent minus 200 mesh coal since the process was originally intended for producing a low-sulfur fuel suitable for pulverized firing in boilers. In earlier work, coal was treated with CaO (the catalyst) in the presence of a solution of NaOH. The results showed that the Battelle process completely eliminated the agglomeration (caking) tendency of highly-caking, Pittsburgh seam coal and greatly increased the hydrogasification and steam gasification reactivities (2). It was also found that the Battelle-treated coal, abbreviated as BTC, was much more reactive than coal impregnated with CaO by slurring with CaO and water at room temperature followed by drying as is conventionally done.

Several catalyst systems have been studied so far. This paper is concerned with further development of the catalyst treatment system consisting of CaO, which is a (hydro)gasification* catalyst for coal, and NaOH which facilitates chemical incorporation of calcium species in coal. Specifically, the paper deals with (a) the effect of particle size of raw coal and catalyst treatment time on hydrogasification properties of BTC, (b) determination of product distribution for (hydro)gasification of BTC, (c) correlation between the properties of batch-produced BTC and continuously-produced BTC, and (d) advantages of using BTC over preoxidized coal.

PROCESS DESCRIPTION

In the case of the catalyst treatment system consisting of CaO and NaOH, the BTC for (hydro)gasification is prepared by four major processing steps. First, the coal of desired particle size is slurried with a mixture of CaO, NaOH, and water. Second, the coal-catalyst slurry is heated to an elevated temperature where it is held sufficiently long to allow chemical incorporation of calcium. Third, the catalyst-impregnated coal is separated and washed to remove excess water and sodium species which can be regenerated and reused. Fourth, and finally, the BTC is dried to the desired moisture level.

During the catalyst treatment, up to 3 percent calcium chemically binds to the coal while a controlled quantity of CaO is physically incorporated throughout the

*The term (hydro)gasification refers in this paper to both hydrogasification and steam gasification of coal.

coal particles. The evidence for chemical incorporation of calcium comes from experiments wherein the BTC was treated with a sugar solution to dissolve the physically-incorporated calcium.

The NaOH apparently helps facilitate the effective penetration and reaction of CaO with coal. It is postulated that NaOH first reacts with coal, opening up its structure and thus facilitating the diffusion of calcium into the coal particles, and then calcium displaces the sodium from coal along with reacting with reaction sites not containing sodium. Usually, a fraction of a percent of sodium remains in BTC after treatment either because of incomplete displacement of chemically-bound sodium by calcium or due to incomplete removal of physically-incorporated sodium by washing. More information on this is provided elsewhere (3).

EXPERIMENTAL DETAILS

The impregnation of coal with catalyst was carried out in a batch reactor system as well as a continuous reaction system called "Miniplant". The (hydro)gasification properties of the BTC produced in these reactor systems were determined in a high-pressure thermobalance (TGA) reactor and in a small, batch-solids fluid-bed gasifier. Table 1 shows the composition of the raw coal, from Montour #4 mine of Pittsburgh #8 seam, used to product BTC.

TABLE 1. COMPOSITION OF RAW COAL

	Weight Percent
<u>Proximate Analysis</u>	
Moisture	0.70
Ash	9.95
Volatile Matter (dry)	37.5
Fixed Carbon (by difference)	51.9
Total	100.0
<u>Ultimate Analysis</u>	
Moisture	0.70
Ash	9.95
Carbon	73.5
Hydrogen	5.25
Nitrogen	1.4
Sulfur	2.6
Oxygen (by difference)	6.6
Total	100.0

Batch Treatment Reactor

The batch experiments on the production of BTC were conducted in a "quick-charge", one-gallon autoclave system shown schematically in Figure 1. In all experiments conducted, the mixture of coal, CaO, and water was heated to the operating temperature and then the NaOH solution was added to the preheated autoclave through the charging bomb. The operating temperature was regained within 3 to 5 minutes after charging NaOH, at which point the zero treatment (retention) time was recorded. Several samples of coal-catalyst slurry were withdrawn and then quickly cooled during an experiment in order to determine the effect of treatment time on properties of BTC.

The catalyst-impregnated (treated) coal was separated from the spent caustic solution and washed under nitrogen with distilled water to remove the excess sodium species and then dried under partial vacuum at 60°C in an inert atmosphere.

Continuous Treatment Reactor (Miniplant)

The experiments on the continuous production of BTC were conducted in the Miniplant system according to the flowsheet shown in Figure 2. The catalyst impregnation took place continuously in a series of stirred-tank reactors, the size and number of which depended on the treatment time and the pumping speed for the coal-catalyst slurry. The nominal pumping speed of the high-pressure pump was 6 gallons per hour. After catalyst impregnation, the product slurry was cooled and then passed through a pressure letdown valve. The BTC was separated from the spent caustic solution (which can be regenerated and reused) in a centrifugal filter, washed with tap water to remove sodium species and then dried in air in a rotary dryer. All processing steps until the first filtration were integrated into continuous operation.

High-Pressure Thermobalance Reactor

The tendency of BTC for agglomeration during hydrogasification and the hydrogasification reactivity relative to raw coal and preoxidized coal were determined in a high-pressure thermobalance reactor (TGA) system described earlier (2). During a thermobalance run, the mass of a coal sample is monitored continuously. From the mass versus time data, the MAF fractional conversion, X , versus time plots are obtained. A convenient way to compare the reactivity of one coal with another is to compare the times, t_x , required for a given fractional conversion, X . An average reactivity of BTC relative to raw coal, R_x , corresponding to a fractional conversion X , may thus be defined as

$$R_x = \frac{(t_x)_{\text{Raw Coal}}}{(t_x)_{\text{BTC}}} \quad 1)$$

Some BTC and raw coal samples had to be pelletized prior to hydrogasification because they were too fine for the 100-mesh basket used for holding the samples. The rest of the samples, containing only a small amount of -60 mesh size particles, were screened to obtain the +60 mesh fraction for the thermobalance experiments.

Batch-Solids Fluid-Bed Gasifier

The batch-solids fluid-bed gasifier system, shown schematically in Figure 3, was used to determine product yield data for (hydro)gasification of BTC and preoxidized coal from the Synthane Process. The reactor tube was 1-1/2-inch I.D. x 3-inch O.D. x 48 inches long. The distributor plate was made of 100-mesh stainless steel screen and placed at the center of the reactor tube.

In all experiments conducted, a 50 g batch of coal was charged through an electrically-operated ball valve in less than 10 seconds to the heated reactor after establishing the desired feed gas rate. The off-gas was allowed to pass through, in order, a hot trap, a water condenser, a water trap, and a cold trap prior to gas analysis. The total volume of the product gas was determined with a dry gas meter. An infrared analyzer (IR) was used to continuously monitor the methane (CH_4) concentration of the product gas. A small bleed stream was taken from the product gas via an isokinetic probe to collect a sample for analysis by a gas chromatograph (GC) at the end of a run. The char was recovered from the reactor at the end of a run and weighed. Also, the weights of the glass wools placed in the hot trap and low-temperature trap were determined before and after a run to determine the yield of tar plus oil.

A carbon balance was made for each run. The product yield data were adjusted to obtain perfect carbon balances.

EXPERIMENTAL RESULTS

Effect of Particle Size and Treatment Time

Earlier work on (hydro)gasification of BTC was done using 70 percent minus 200 mesh coal. However, because of the problem in using 200 mesh or finer coal for the fluid-bed gasifier, it was desirable to know the effect of catalyst treatment time on the (hydro) gasification characteristics of BTC produced from coarser raw coal. Therefore, experiments were conducted on coals with particle size ranging from 6350 μm (0.25 inch) to 74 μm (200 mesh). The catalyst treatment was carried out at 250°C, in the presence of a solution of NaOH, using a CaO/coal ratio of 0.13. The experiments were conducted on coal ground and screened to the following sizes: 0.25 inch to 0.187 inch (4 mesh); -20+28 mesh; -35+48 mesh; -65+100 mesh; -150+200 mesh; and 70 percent -200 mesh. While nearly all of the calcium remained in the BTC, the sodium content increased from about 0.1 percent of MAF coal for 200 mesh coal to about 0.8 percent for 20 mesh coal due to inefficient washing of larger particles (3).

To illustrate the dependence of hydrogasification reactivity on coal particle size and coal treatment time, the time required to hydrogasify 50 percent of the MAF BTC is shown in Figure 4 as a function of coal treatment time and coal particle size. Figure 4 shows that the reactivity increases with treatment time, leveling off a value that does not seem to depend on the particle size. However, the time required to achieve maximum reactivity increases with particle size. For example, a treatment time of about 10 minutes is sufficiently long to achieve near-maximum reactivity with 70 percent minus 200 mesh coal, while 20 minutes are required to achieve nearly the same reactivity with -20+28 mesh coal. The BTC produced from 0.25-inch to 0.187-inch size raw coal was not hydrogasified since the particles were too large for the thermobalance reactor.

Figure 5 shows the complete thermobalance data for raw coals of different particle sizes as well as for BTC produced from these coals. For the treated coals, the time of treatment was 60 minutes which, according to the data shown in Figure 4, was longer than necessary. The reason for the somewhat higher reactivity for the coarser coal is that it was not pelletized which can lower the reactivity, depending on the compaction pressure used for pelletization. Figure 5 indicates the potential that treatment has for reducing the total reactor volume in a gasification plant. For example, if one assumes a 20-minute coal residence time is required for treatment, Figure 5 indicates the resulting BTC can be hydrogasified to a 65 percent conversion level in less than 3 minutes, while raw coal requires 90 minutes for the same level of conversion. Thus, the total volume required for treatment plus hydrogasification should be considerably less for BTC than for raw coal.

The data in Figure 5 show that the value of the average relative reactivity R_x , defined in Equation 1, increases with X . For example, for BTC from -20+28 mesh raw coal, the values of R_x at X equal to 0.5, 0.6, and 0.7 are 17, 29, and 49, respectively. This is due to the fact that raw coal is deactivated while BTC is not during hydrogasification, as discussed later.

The increase in hydrogasification reactivity due to treatment was found to be accompanied by a reduction in the tendency for agglomeration during hydrogasification and at the treatment time required to achieve maximum reactivity, the agglomerating tendency was completely eliminated. For example, treatment of -20+28 mesh coal for 20 minutes produced a completely nonagglomerating BTC, and treating the same raw coal for 11 minutes produced a BTC that had a slight tendency for agglomeration, while the raw coal had a severe tendency for agglomeration. Furthermore, it was found that coarser particles required a longer treatment time to completely destroy the agglomerating tendency of coal. For example, a treatment time of 10 minutes was sufficient to completely eliminate the agglomeration tendency of 70 percent minus 200 mesh coal, while BTC produced from -20+48 mesh coal after treatment for 11 minutes still had a slight tendency for agglomeration.

The free swelling index (FSI) of BTC treated for 120 minutes and raw coals were also determined in this study. The rationale for doing this was that FSI determination is easy and quick and that a zero value for FSI is a necessary (but not sufficient) condition for completely destroying the agglomeration tendency during hydrogasification. It was found that the FSI of raw coal particles as large as 0.25 inch could be lowered from 8 to 0 by the Battelle treatment. The treatment of 0.25-inch size particles was carried out to determine if the Battelle treatment could be used to produce nonagglomerating feedstock for moving-bed gasification systems such as Lurgi. The material balance data for treatment experiments showed that there was no loss of volatile matter or carbon, within errors of measurement, during catalyst treatment. On the other hand, preoxidation, which is commonly employed for reduction of FSI of coal, results in the loss of 20 percent or more volatile matter.

It should be pointed out that the CaO/coal ratio of 0.13, used in the above experiments, was about two times the ratio necessary to achieve maximum hydrogasification reactivity.

The steam gasification reactivity of BTC was not determined in the thermobalance because maximum steam gasification reactivity is achieved before maximum hydrogasification reactivity. Earlier data with fine coal showed that BTC having maximum steam gasification reactivity can be gasified at 675°C at about the same rate as raw coal at 850°C (2). (The activation energy for steam gasification of BTC was found to be 23 kcal/mole.) Based on earlier data, the times required for a fractional conversion of 0.7 at 850°C and 500 psig for raw coal and BTC (having maximum-possible hydrogasification reactivity) are expected to be about 50 minutes and 5 minutes, respectively.

Fluid-Bed Data for (Hydro)gasification of BTC and Preoxidized Coal

Experiments were conducted in a batch-solids fluid-bed gasifier to determine product distribution for BTC gasified with hydrogen, steam, and hydrogen plus steam. Because of the small size of BTC used (about 50 g) and because of problems with batch operation, only the carbon balance data could be obtained with reasonable accuracies. The results showed that not only the (hydro)gasification reactivity of BTC was as high as indicated by thermobalance data, but also that the yields of ethane (C_2H_6) and ethylene (C_2H_4) were much greater than observed with raw coal or preoxidized coal in commercial or advanced coal gasification processes.

Data were also obtained on the gasification of preoxidized coal from Synthane Process to make a direct comparison between the (hydro)gasification properties of BTC and preoxidized coal.

Hydrogasification Data. The yield data for three typical runs with BTC and one run with preoxidized coal are summarized in Table 2. These data show that under comparable treatment conditions, the total carbon conversion is much greater for BTC than for preoxidized coal because of the higher hydrogasification reactivity of BTC. The relative reactivity of BTC is actually much greater than may be apparent from the total carbon conversion data because most of the carbon gasified in the case of the preoxidized coal is actually the volatile carbon. In fact, it can be shown that the base carbon conversion for BTC in Table 2 is more than about three times that for preoxidized coal. The high hydrogasification reactivity of BTC compared to preoxidized coal is also demonstrated by the thermobalance data plotted in Figure 6. It can be seen from Figure 6 that the time for 70 percent conversion of MAF coal is less for BTC even though preoxidized coal is hydrogasified at 50°C higher in temperature and at 4 times the hydrogen partial pressure (i.e., 1000 psig versus 250 psig).

One of the most interesting observations in this study was that a very significant amount of carbon was converted to C_2H_4 and C_2H_6 . For example, the combined conversion of carbon to C_2H_4 and C_2H_6 in Runs Nos. 9, 12, and 13 were 13.1, 22.3, and 14.4 percent, respectively. In fact, in Run No. 12, there was more carbon converted to C_2H_4 plus

C₂H₆ than to CH₄. The conversion of so much carbon to C₂H₄ and C₂H₆ is unusual since in most of the advanced gasification processes, such as Synthane and Hydrane, the fraction of coal carbon converted to these species is only a couple of percent. Indeed, the data in Table 2 for preoxidized coal show that the combined yield of C₂H₄ and C₂H₆ was only 2.3 percent. The rates of production of C₂H₄ and C₂H₆ were found to be negligible after the first one and one-half minutes in all runs. Thus, the C₂ hydrocarbons are formed primarily during hydrogasification of the most reactive carbon. The yields of these hydrocarbons were found to be lower at higher temperatures.

At this stage, the results on the yields of C₂H₄ and C₂H₆ should be interpreted cautiously because of differences expected in the coal heat-up rates and gas-phase residence time between the batch-solids gasifier and a continuous gasifier.

It should be pointed out that isothermal operation could not be achieved during hydrogasification runs because of unsteady state operation and because the hydrogasification reaction is highly exothermic. The methane concentrations in the off-gas during a run was as high as 35 percent by volume which occurred at about one minute after charging coal to the gasifier. The temperature was highest at the point of maximum rate of methane production.

TABLE 2. COMPARISON OF YIELDS FOR HYDROGASIFICATION OF BTC AND PREOXIDIZED COAL

Fluid-Bed Run No.	BTC (-20+28 mesh Raw Coal created for 20 minutes)			Preoxidized Coal (+65 mesh)
	9	12	13	15
Total Pressure, psia	265	265	290	265
P _{H₂} in Feed Gas, psia	265	265	290	265
Temperature Range, °C	755-1045	750-850	880-1090	850-930
Reaction Time, minutes	13	10	10	12
<u>Carbon Conversion, wt %</u>				
CH ₄	36.6	17.5	39.0	21.2
C ₂ H ₄	2.0	10.1	6.0	0.3
C ₂ H ₆	11.1	12.2	8.4	2.0
Tar and Oil	5.2	6.2	4.1	3.0
Oxides	4.3	5.6	4.4	3.5
Total	59.2	51.6	61.9	30.0
Percent Carbon Converted to C ₁ +C ₂ Hydrocarbons	49.7	39.8	53.4	23.5

The temperature dependence for the specific rate of methane production in the post-devolatilization region is shown in Figure 7. These data were generated from one fluid-bed run since temperature was not constant. The straight line for Arrhenius plot suggests that there is no deactivation of BTC during hydrogasification in the carbon conversion range of 40 to 55 percent, verifying results from thermobalance data discussed later. The rates in Figure 7 were corrected for variation of partial pressure of hydrogen during the run using the first-order power law dependence for hydrogen partial pressure found from thermobalance data. The rate expression for specific rate of carbon conversion to methane in the post-devolatilization region is

$$-\left(\frac{1}{1-X_c}\right) \frac{dX_c(\text{CH}_4)}{dt} = 88 (P_{\text{H}_2}) \exp (-13,800/T) \quad (2)$$

where, t is the time in minutes, P_{H_2} is in psia, T is the temperature in degrees kelvin, X_c is the total carbon conversion, and $X_c(\text{CH}_4)$ is the fraction of carbon converted to CH₄. Equation 2 should be valid up to a value of X_c of about 0.65 to 0.70 at a hydrogen partial pressure of 225 psia and to X_c values greater than 0.7 at higher pressures.

The data in Figure 7 show that the batch fluid-bed data, that have been corrected for the presence of as much as 15-20 percent methane, correlates well with thermobalance data. For the thermobalance data, the specific rate of MAF coal conversion was used, which is nearly the same as the left-hand side of Equation 2 in the post-devolatilization region.

The fractional conversion of carbon to tar plus oil was found to vary between 4 and 7 percent for runs with BTC using hydrogen as a feed gas. The yield of tar plus oil was found to decrease with temperature as found by other investigators (4). It is expected that the yield of tar and oil from BTC will be lower in a continuous fluid-bed gasifier where the coal can be introduced into the fluid bed directly and in which the coal can be heated very rapidly. The composition or the quality of tar and oil formed from BTC could not be determined because of the small amounts of samples available. It is expected though, based on our work on the pyrolysis of BTC, that the organic liquids (tar and oil) from BTC are significantly lower boiling than the organic liquids from untreated raw coal.

There was little or no H_2S detected by GC in off-gas from gasification of BTC. Furthermore, sulfur analysis of BTC and char showed that more than 90 percent sulfur was retained in the char during hydrogasification. It is believed that sulfur in char is present as CaS .

Steam Gasification Data. Table 3 summarizes typical yield data for BTC gasified with steam and steam plus hydrogen along with data for gasification of preoxidized coal (from Synthene Process). The data for Runs Nos. 14 and 16 show that the steam gasification reactivity of BTC is much greater than that of preoxidized coal as expected. Also, the rate of hydrocarbon formation and the ratio of C_2 hydrocarbon yield to CH_4 yield for BTC is greater than for preoxidized coal.

TABLE 3. COMPARISON OF YIELDS FOR GASIFICATION OF BTC AND PREOXIDIZED COAL WITH STEAM AND STEAM PLUS HYDROGEN

Fluid-Bed Run No.	BTC (-20+28 mesh Raw Coal treated for 20 minutes)		Preoxidized Coal (+65 mesh)	
	14	17	16	19
Total Pressure, psia	255	205	215	205
P_{H_2} in Feed Gas, psia	0	111	0	111
P_{H_2O} in Feed Gas, psia	66	94	57	94
P_{He} in Feed Gas, psia	189	0	158	0
Temperature Range, °C	785-795	780-800	800-810	850-890
Reaction Time, minutes	12	12	14.5	17
<u>Carbon Conversion, wt %</u>				
CH_4	10.6	25.9	7.1	15.1
C_2H_4	2.1	2.0	1.0	0.2
C_2H_6	2.1	4.6	0.5	0.8
Tar + Oil ^(a)	4.2	1.9	2.5	0.6
Oxides	79.0	47.2	14.2	11.3
Total	98.0	81.6	25.3	28.0
Percent Carbon Converted to C_1+C_2 Hydrocarbons	14.8	32.5	8.6	16.1

(a) Underestimated because some oil was condensed in the steam condenser.

Runs Nos. 17 and 19 were conducted with steam-hydrogen mixtures in order to simulate more closely the conditions in a continuous, steam-oxygen, fluid-bed gasifier. Again, BTC is found to be more reactive and more selectively gasified to C_2 hydrocarbon than preoxidized coal. Note that the Yield of C_2 hydrocarbons and CH_4 increases with hydrogen partial pressure in the range studied. For example, the yield of C_2 hydrocarbon

in Run No. 14 (in which the partial pressure of H_2 in the off-gas was 15 psia) was 4.2 percent, in Run No. 17 ($P_{H_2} = 111$ psia) it was 6.6 percent, and in runs with pure hydrogen ($P_{H_2} = 265$ to 290 psia) it varied from about 13 to 22 percent.

The rates of production of various gases during Run No. 17 ($P_{H_2} = 111$ psia) are plotted in Figure 8. Integration of these rate data to various levels of carbon conversion showed that all the C_2 hydrocarbons and about 95 percent of the CH_4 were produced during the gasification of the initial 55 percent of carbon. Thus, the combined yield of C_1 and C_2 hydrocarbons, or what may be called "equivalent CH_4 ", will be 31-32 percent for 60-70 percent total carbon conversion. On the other hand, extrapolation to 60 percent carbon conversion of the rate data for preoxidized coal (Run No. 19) showed that the combined yield of C_1 and C_2 hydrocarbons was 20.5 percent.

The batch fluid-bed data for preoxidized coal were extrapolated to estimate the equivalent CH_4 yield corresponding to the operating conditions employed in the 4-inch I.D. Synthane gasifier operating at 570 psig. The estimated value was 15.8 percent which corresponds well with the 15.2 percent actually observed (5,6). Using a similar estimation procedure for BTC, the equivalent CH_4 yield for a single-stage, fluid-bed, steam-oxygen gasifier operated at 750°C and 300 psig was projected to be in the neighborhood of 26 percent. (The minimum equivalent CH_4 yield for BTC should of course be 14.8 percent, as determined from Run No. 14, corresponding to P_{H_2} equal to 15 psia only.) Thus, the equivalent CH_4 yield for BTC is expected to be significantly higher for BTC than for preoxidized coal for single-stage, steam-oxygen gasification.

The data in Table 3 show that steam gasification of BTC can be carried out at a reasonable rate at a temperature well below 790°C, as also found earlier (2). The data in Table 3 also illustrate the suppressive effect that increasing the hydrogen partial pressure has on steam gasification rate of BTC. This effect has been noted by other investigators (7,8). The simplest physical explanation for the lowering of the steam gasification rate by hydrogen is that the hydrogen adsorbs on reaction sites making them unavailable to steam.

As in the case of hydrogasification, little or no H_2S was detected in the off-gas during steam gasification of BTC, indicating that sulfur was captured by CaO (probably as CaS). The advantage of retaining sulfur in the char as CaS is that the char can be burnt in an environmentally-acceptable manner to provide for the energy requirements of the gasification plant.

Continuous Production of BTC

The objectives behind continuous production tests for production of BTC were to establish that BTC could be produced continuously and to establish the correlation between batch and continuous (Miniplant) tests.

It was found that BTC, having hydro(gasification) properties superior to raw coal, could be produced from coarse as well as fine coal on a continuous basis. The (hydro) gasification properties of Miniplant-produced BTC were found to be the same as for batch-produced BTC. For example, the thermobalance data in Figure 9 show that the hydrogasification reactivity of Miniplant-produced BTC was the same as for batch-produced BTC. Furthermore, data from batch-solids fluid-bed gasifier showed that the distribution of the products from (hydro)gasification was nearly independent of the type of reactor used for production of BTC.

Hydrogasification Rate Analysis

An interesting finding in this study was that there was no deactivation of BTC during hydrogasification, in the post-devolatilization regime, up to an MAF fractional conversion of about 0.75. On the other hand, the rate of hydrogasification of raw coal was found to decline more or less exponentially in the post-devolatilization regime. This remarkable difference between the hydrogasification properties of BTC and raw

coal is illustrated in Figure 10 where the specific rate of hydrogasification, defined as $(-dX/dt)/(1-X)$, is plotted against X, where X is the fractional conversion of MAF coal. (It is not clear whether the higher initial devolatilization rate for BTC is due to higher reactivity or simply faster heat-up because the BTC particles remained discrete while the raw coal particles expanded into a sponge-like mass.) Figure 10 shows that the reactivity of BTC relative to raw coal increases with X. The decline in specific rate of hydrogasification with increasing conversion for the raw coal is a clear indication of decreasing reactivity brought about by the increasing graphitization that occurs in the untreated coal. That graphitization occurs has become very widely accepted among investigators in this area. Thus, it may be speculated that the chemical incorporation of the catalyst prevents graphitization of BTC during hydrogasification to a fractional conversion of about 0.75. Wood (9) and Gardner (10) have also reported lowering of the tendency for deactivation of coal in the presence of a catalyst. However, their catalysts were much less effective than the catalyst in BTC because their catalysts were only physically and (probably) less-effectively incorporated in coal.

The reason for decline in the specific rate for BTC after X equal to 0.75 is not understood. But this may suggest an alternate hypothesis for the role of the catalyst in BTC. It may, for example, be hypothesized that the role of the catalyst is to simply extend the limit for rapid rate methanation stage for base carbon conversion proposed by Johnson (7) and others (11).

CURRENT STATUS OF PROGRAM

Under current ERDA sponsorship, several catalyst systems are to be evaluated as alternatives to the system comprising of NaOH and CaO. The objective is to minimize the cost of SNG or medium-Btu gas production from high-sulfur caking coals.

Presently, the catalyst system comprising of CaO alone is being evaluated in detail. Since no NaOH is required in this process, there is no need for washing of BTC or regeneration of spent leachant. Furthermore, the high-pressure slurry containing BTC, water and the catalyst may be slurry-fed to a gasifier. The results to date with the CaO system have been very encouraging.

CONCLUSIONS

The data on the Battelle treatment of coal with CaO in the presence of NaOH shows that nonagglomerating BTC having a very high (hydro)gasification reactivity compared to raw coal can be produced from raw coal particles as large as 20 mesh. The maximum-possible hydrogasification reactivity of BTC is independent of raw coal particle size. But, -20+28 mesh coal requires about twice as long a treatment time as 70 percent minus 200 mesh coal to achieve the maximum-possible reactivity. The increase in the reactivity of coal due to treatment is accompanied by a decrease in the tendency for agglomeration during hydrogasification. And, at the treatment time required to achieve maximum reactivity, the agglomeration tendency is completely eliminated. The FSI of coal particles as large as 0.25 inch from Pittsburgh #8 seam is found to be reduced from 8 to 0 due to Battelle treatment.

It has been established that the BTC produced in a continuous treatment plant has the same (hydro)gasification properties as BTC produced in a batch reactor.

Comparison of (hydro)gasification properties of BTC and preoxidized coal from Synthane Process shows that (a) (hydro)gasification reactivity of BTC is much higher, (b) (hydro)gasification of BTC yields substantially greater quantities of C_2H_4 and C_2H_6 , and (c) the equivalent CH_4 yield for BTC is significantly higher for steam gasification. The BTC also retains most of the sulfur in char, probably in the form of CaS, during (hydro)gasification. Thus, combustion of char from BTC is not expected to require an SO_2 scrubber.

The hydrogasification rate analysis of the data shows that there is no deactivation of BTC during hydrogasification in the post-devolatilization regime up to a fractional conversion of 0.75 while raw coal reactivity declines almost exponentially with X.

The above advantages of BTC over raw coal and preoxidized coal suggest that Battelle catalyst treatment should allow more reliable, environmentally-acceptable and more economic utilization of high-sulfur, Eastern U.S. coals.

ACKNOWLEDGEMENTS

The authors wish to express their appreciation to Mr. Gary Felton for providing help in designing the batch-solids fluid-bed gasifier, to Mr. Sam Tam for carrying out the Miniplant tests, and to Mr. Herm Nack for his continued interest and valuable suggestions. The financial support for this study was provided by ERDA.

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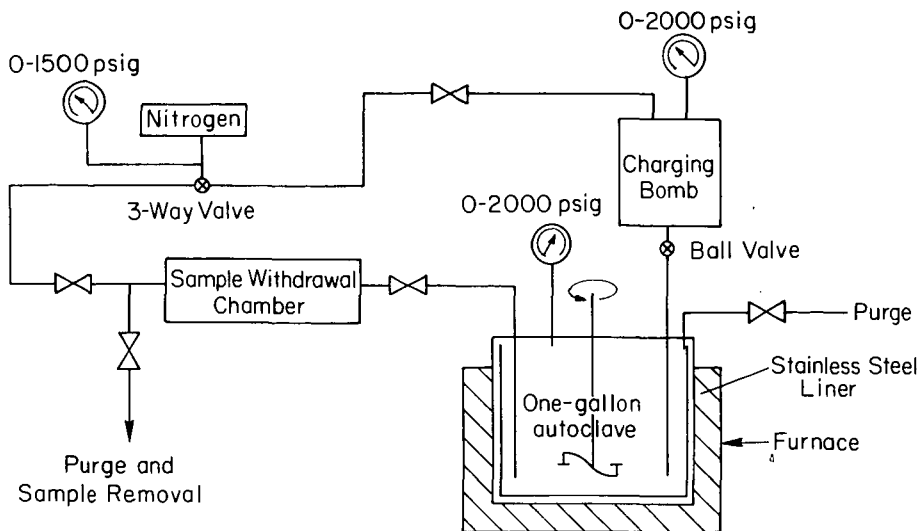


FIGURE 1. SCHEMATIC DIAGRAM OF THE BATCH REACTOR SYSTEM FOR PRODUCTION OF BTC

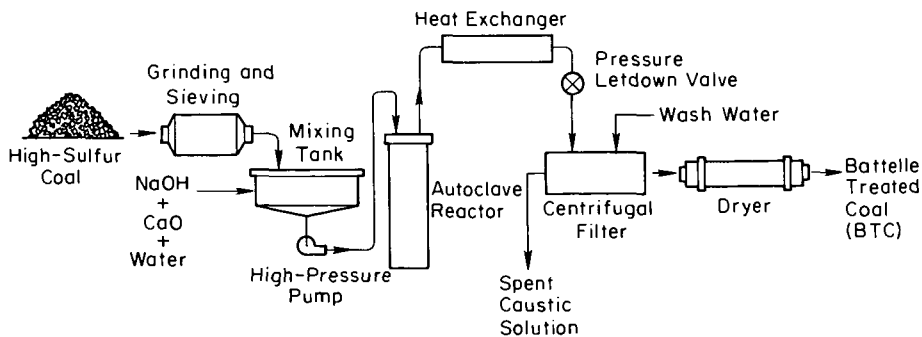


FIGURE 2. FLOWSHEET OF PROCESS FOR PRODUCTION OF BTC IN THE CONTINUOUS REACTOR (MINIPLANT)

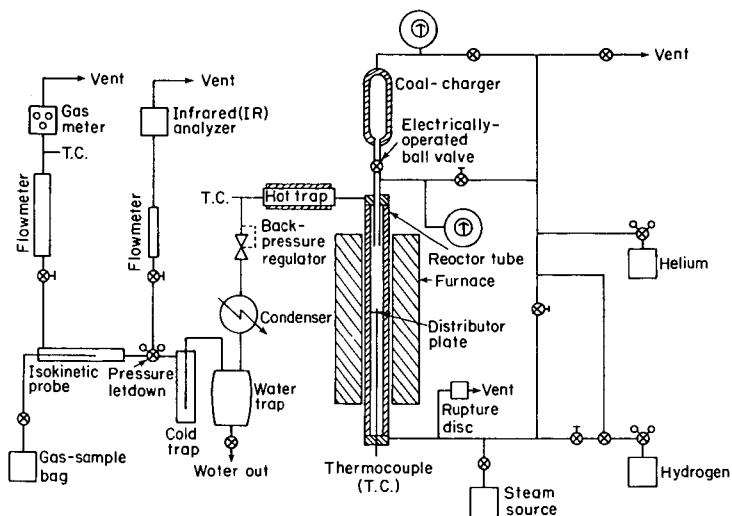


FIGURE 3. SCHEMATIC OF THE BATCH-SOLIDS FLUID-BED GASIFIER

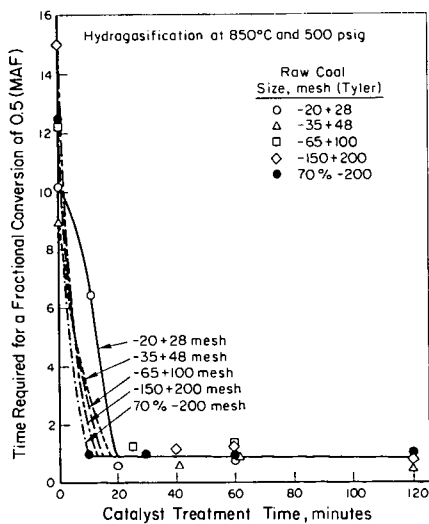


FIGURE 4. DEPENDENCE OF THE TIME REQUIRED FOR A FRACTIONAL CONVERSION OF 0.5 FOR HYDROGASIFICATION OF BTC ON PARTICLE SIZE OF RAW COAL AND CATALYST TREATMENT TIME

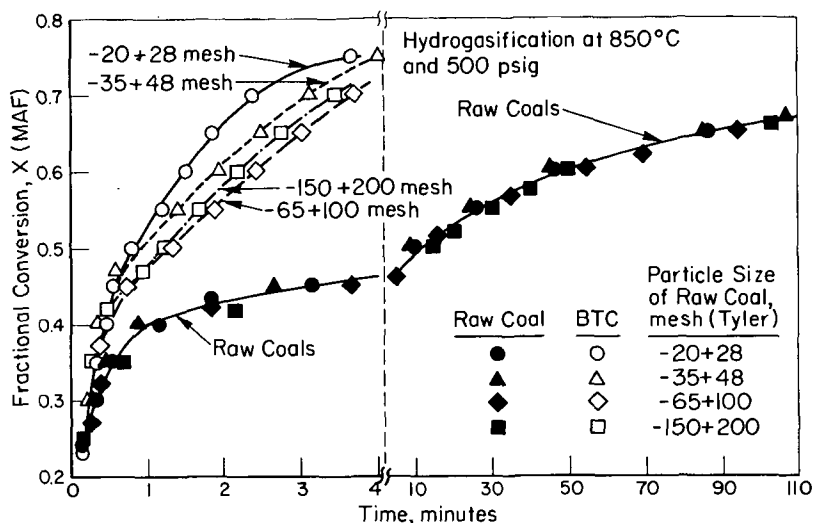


FIGURE 5. EFFECT OF RAW COAL PARTICLE SIZE ON THE HYDROGASIFICATION REACTIVITY OF BTC RELATIVE TO RAW COAL. CATALYST TREATMENT TIME = 60 MINUTES

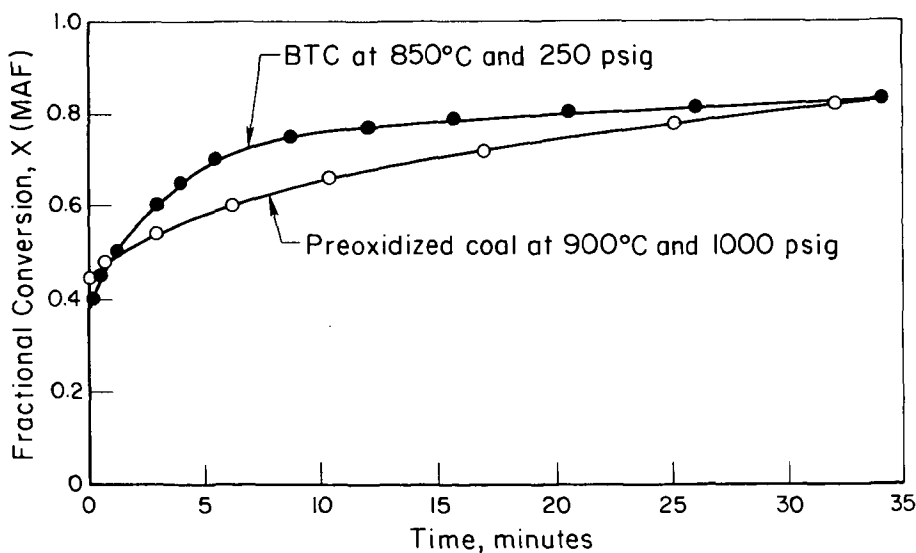


FIGURE 6. COMPARISON OF THE HYDROGASIFICATION REACTIVITY OF BTC (TREATMENT TIME = 20 MINUTES) WITH PREOXIDIZED COAL

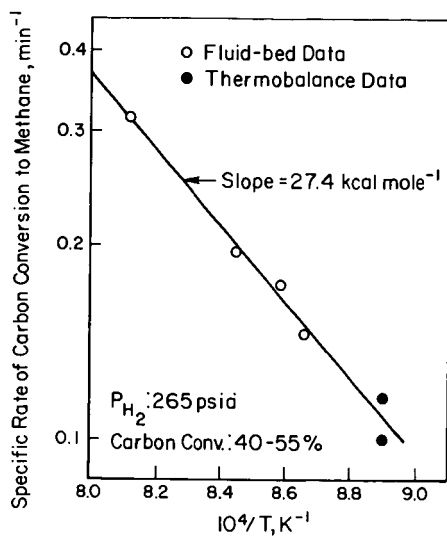


FIGURE 7. ARRHENIUS PLOT FOR SPECIFIC RATE OF CARBON CONVERSION TO METHANE FOR BTC (FLUID-BED RUN NO. 13)

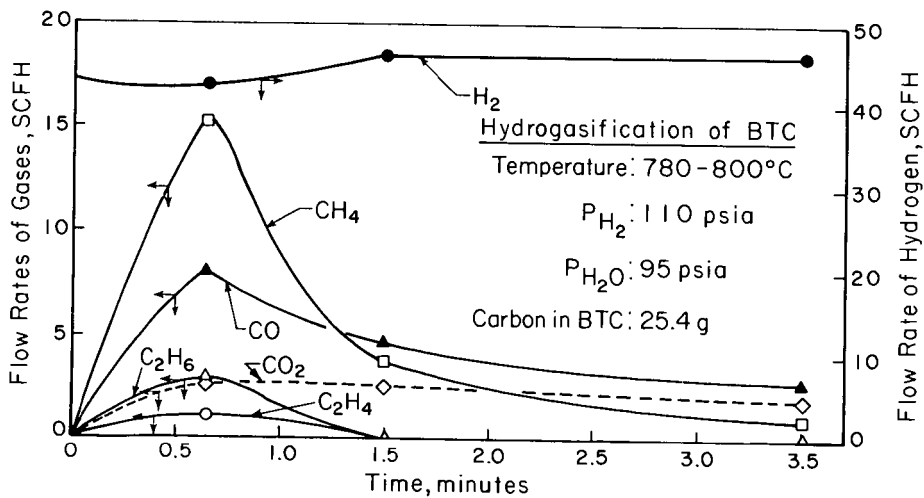


FIGURE 8. FLOW RATES OF VARIOUS GASES EXITING FROM THE FLUID BED DURING GASIFICATION OF BTC WITH STEAM PLUS HYDROGEN (FLUID-BED RUN NO. 17)

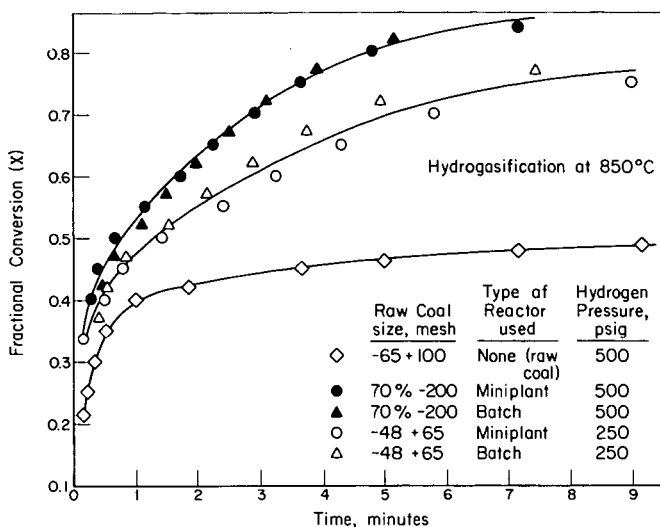


FIGURE 9. COMPARISON OF THE HYDROGASIFICATION REACTIVITY OF BTC PRODUCED IN THE MINIPLANT WITH THE REACTIVITY OF RAW COAL AND BTC PRODUCED IN THE BATCH AUTOCLAVE (CATALYST TREATMENT TIME = 20-35 MINUTES)

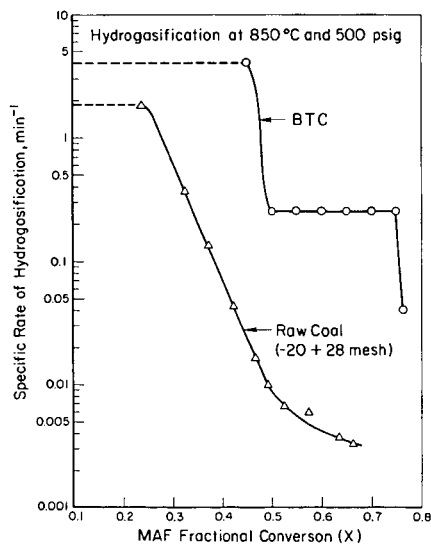


FIGURE 10. PLOTS OF THE SPECIFIC RATE OF HYDROGASIFICATION VERSUS FRACTIONAL CONVERSION FOR RAW COAL AND BTC (TREATMENT TIME = 20 MINUTES)